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Persistent Spectral Hole-Burning: Photon-Gating and Fundamental Statistical Limits

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1. INTRODUCTION

Persistent spectral hole-burning (PSHB) [1] is a process whereby "marks", or "holes", are made in the inhomogeneously broadened absorption line of guest centers in an amorphous or crystalline host matrix by frequency-selective photochemistry and/or photophysics. PSHB is an active area of current research for two main reasons: (1) spectral holes are uniquely sensitive probes of guest-host interactions, perturbations by external fields, and the complex distributions characteristic of polymers and glasses[2], and (2) the presence or absence of spectral holes may in the future be used to store digital data in an extremely high density frequency domain optical storage system (FDOS)[3].

If one steps back from the detailed PSHB properties of a single material, several general limits on the PSHB process may be recognized. To be useful for optical data storage where bits are stored in focused spots and read out by scanning a tunable laser[4], it seems fairly clear that single-photon processes have severe signal-to-noise limitations[5] and therefore must be replaced by gated hole-burning mechanisms that can be read nondestructively[6]. Another fundamental limit derives from the recently-observed statistical fine structure (SFS)[7], an intrinsic property of all inhomogeneously broadened lines, which represents the shallowest spectral feature that can be detected within such lines. A third limiting regime for PSHB is suggested by recent measurements [8] of the optical spectrum of a single molecular impurity in a solid: can PSHB occur for one, single impurity center, yielding true molecular or atomic storage?

2. LIMITATIONS ON SINGLE-PHOTON MECHANISMS

Turning first to the limits of single-photon mechanisms for frequency-domain optical storage applications, it must be recognized from the outset that the utility of a particular material for FDOS depends somewhat upon the actual storage configuration. For the case of frequency-scanned readout in small focused spots, single-photon processes provide sufficient signal-to-noise ratio only over a very limited parameter space[5]. For definiteness, we assume the following about the optical storage system: (i) the writing and reading times are on the order of 30 ns/bit, (ii) the focal volume in which many frequency-domain bits are stored is 10 μm in diameter by 100 μm thick, and (iii) the readout signal-to-noise ratio must be greater than or equal to 26 dB in the full reading bandwidth. The key point is that all these properties must be present *simultaneously*: the material must have the ability to form deep holes in short burning times and yet allow fast reading at high signal-to-noise ratios with focused beams. These reasonable requirements place several well-defined constraints on the dynamical properties of the hole-burning mechanism.

For example, a material with low hole-burning efficiency would be quite easy to read without serious destruction of the written holes, but such a system would be difficult to write with high contrast in short burning times. Conversely, a system that shows fast burning due to a high quantum efficiency for hole production would be difficult to read without burning of the unwritten centers by the tightly focused reading beam. Thus, the essential problem with single-photon processes is that there is no threshold in the hole formation mechanism. The process of hole detection requires the absorption of photons by the remaining unburned centers, and if high powers are necessary to detect the dip in the absorption line with adequate signal-to-noise, the hole pattern can be destroyed by the reading laser beam (i.e., a "trench" can be formed over the spectral region probed by the reading laser).

To understand this problem more fully, we review an analysis[5] of the coupled reading-writing problem in small spots for materials with monophotonic or single-photon hole-burning mechanisms. The material is characterized by two microscopic parameters: the peak low temperature absorption cross section σ, and the hole-burning quantum efficiency η[9]. The plan of the analysis involves using simple rate equations to compute the largest hole depth that can be produced in 30 ns. Then one computes the read signal from the resulting hole (in transmission) for a 30 ns reading time, requiring that the readout SNR is large enough for practical digital data retrieval. The deepest hole that can be burned in 30 ns has relative depth near η, because with excited state lifetimes on the order of 10 ns, each center can absorb at most only a few photons. During reading, the detection process is assumed to be quantum (shot) noise limited, and the reading laser power is increased until the required SNR of 26 dB in 16 MHz bandwidth is reached, or until power broadening occurs due to saturation. The resulting SNR can be expressed as

$$\mathrm{SNR} = (\eta_Q \Gamma_R \Lambda \tau_R/2)^{1/2}\, \eta \alpha_o L \exp(-\alpha_o L/2), \tag{1}$$

where η_Q is the detection quantum efficiency, Γ_R is the reading photon flux, Λ is the laser spot area, τ_R is the reading time, L is the sample length, and α_o is the initial absorption coefficient before burning. This is the SNR for the first read expressed in terms of a current ratio (or equivalently, voltage ratio across a fixed resistance).

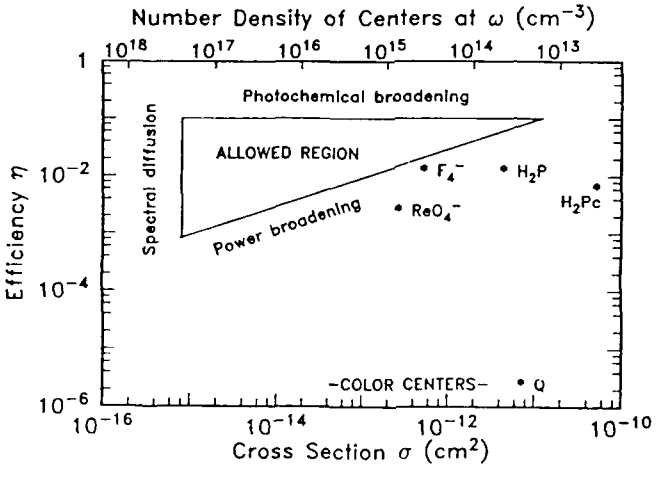

Fig. 1 Allowed region of efficiency η, number density of centers at ω, and cross section σ in order for the first read to yield acceptable SNR. The various abbreviations are defined in Ref. [5].

Figure 1 shows the region in the $\eta - \sigma$ plane in which Eq. (1) yields SNR > 20 (voltage ratio). The analysis assumes that the sample absorptivity has been previously set to the value $\alpha_o L = \sigma N_\omega L = 2$ which can be shown to yield the optimum SNR [5]; hence the concentration of centers N_ω necessary to keep α_o fixed (top axis) must decrease as the cross

section increases. The concentration N_ω refers to the number density of centers within one homogeneous linewidth of the burning laser frequency ω; the total concentration of centers would be larger approximately by the ratio of the inhomogeneous to homogeneous widths. The triangular region in the figure represents the class of materials that would yield acceptable signal-to-noise ratios for the first read after burning a single hole. This means that a useful single-photon material must have *low* absorption cross section and *high* quantum efficiency, with sufficient solubility in the host to permit the concentrations shown on the upper axis. The boundaries of the allowed region are defined by an upper limit on the practical value of η that can be reached without hole broadening due to excessive photochemistry, an upper limit on the tolerable density of centers at ω without undesirable intercenter interaction, and the requirement that during readout the reading intensity be kept below the saturation intensity for the transition. The various symbols locate a representative class of previously studied single-photon materials, none of which fall within the allowed region for the first read.

So far, only the SNR requirements for the first read directly after writing have been considered. However, one realizes very quickly that at the power levels required to achieve usable SNR, the entire absorption line scanned by the reading laser is gradually burned away during each successive read. It is possible to determine M^*, the number of reads that can be achieved for each $\eta - \sigma$ pair before the SNR drops to unacceptable levels (see Ref. [5]). Near the power broadening boundary line and in the upper right portion of the allowed triangle in Fig. 1, the number of reads is fairly small and a practical storage system based on such materials would require excessive refreshing capability. Much better performance results in the upper left corner, i. e., at high quantum efficiency and low absorption cross section. From the physical point of view, high η is needed so that the hole produced in the 30 ns burning time is as deep as possible, thus less reading laser power is required. Low cross section means that more photons pass by a given center without absorption, and these photons can then improve the SNR at the detector. For materials in the upper left corner of the triangle with η near 0.1 and σ near 10^{-15} cm^2, thousands to tens of thousands of reads can be achieved before refresh is required.

The results in Figure 1 show that a well-defined challenge exists for scientists in the field of PSHB: find single-photon materials that have values of quantum efficiency and cross section that fall within the allowed region, as well as solubilities that allow concentrations shown along the top axis. One might look for hole-burning in partially allowed transitions, such as n-π^* transitions of organic molecules and d-f transitions of divalent rare earth systems. However, the parameter space of useful η-σ values is somewhat small. This is a result of the unfortunate fact that detection of spectral hole means measuring the absorption from centers that have *not* left the inhomogeneous line. In other words, writing of unwritten centers can occur during reading, and this problem is most severe under the conditions of

high data rates with tightly focused laser spots. Such a limitation with single-photon processes is not too surprising when one recognizes that essentially all currently practical long-term storage technologies feature some type of hysteresis or threshold in the storage mechanism.

3. PHOTON-GATED PROCESSES FOR PERSISTENT SPECTRAL HOLE-BURNING

The lack of a threshold in single-photon processes for PSHB prompted a search in many laboratories for gated PSHB mechanisms, where a secondary gating field in addition to the frequency-selecting light beam must be present for persistent spectral hole formation. In the class of *photon-gated* mechanisms[6], a secondary light field usually at a different wavelength is required for the photoreaction leading to writing.

The first requirement for gating is that irradiation with the frequency-selective wavelength causes no persistent photoinduced change in the absorbing center. However, when the center has been placed in the excited state by absorption of a frequency-selecting photon *and* an external "gating" photon is present, a photoinduced change occurs and the center enters a new ground state or permanent reservoir that no longer absorbs at the site-selecting wavelength. The "dip" or region of reduced absorption that is left behind in the inhomogeneous line is the resulting spectral hole that can be detected nondestructively by scanning the frequency-selecting wavelength and measuring the absorption (i.e., by the ground state population that has not reacted). In this manner, gated mechanisms add a crucial threshold to the hole formation process, which allows the writing and reading processes to be uncoupled.

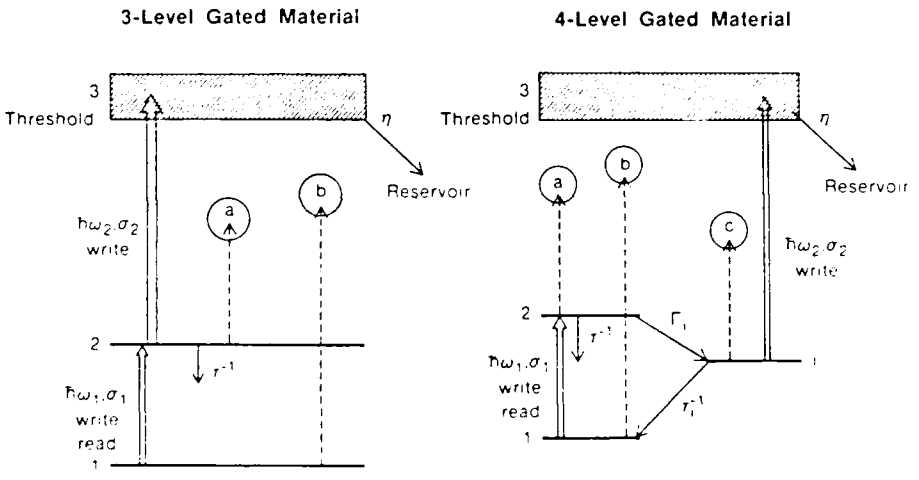

Fig. 2 (a) Optimal level structure of a three-level photon-gated PSHB mechanism. The absorption should be small in the circular regions. (b) Optimal level structure of a four-level photon-gated PSHB mechanism.

Figure 2 illustrates some general requirements on three-level and four-level photon-gated PSHB mechanisms in order to achieve high overall efficiency and high gating ratio, where the gating ratio is a measure of the efficiency of two-color hole production divided by the efficiency of one-color hole production with λ_1 alone[10]. While the exact materials requirements depend strongly upon the actual system configuration and signal-to-noise requirements, some general comments about the required level structure can be made.

The left side of Fig. 2 illustrates the three-level system which is the common configuration for many inorganic materials. A first requirement is that λ_1 should be larger than λ_2, so that the site-selecting beam cannot also easily act as the gating beam. The absorption in the circular regions should be small to reduce one-color burning (by three λ_1 photons, case a) or bleaching by the gating light (by two λ_2 photons, case b). The lifetime τ of the intermediate state 2 should be long enough to allow large populations to build up in this state for further excitation to the reactive levels 3. In cases where τ is much larger than the data access time the storage material does not have to be exposed to both photon energies simultaneously. Further, there is no fundamental need for a frequency-selective narrow-band transition from level 2 to level 3; however, in certain instances, narrow-band levels 3 involving transitions with high peak cross sections may be preferable to a continuum absorption such as a conduction band. The microscopic yield η from the reactive levels 3 should be as large as possible for high overall gating efficiency.

In principle, systems with $\lambda_1 = \lambda_2$ can exhibit gated PSHB in the sense that the hole-burning yield is nonlinear with laser intensity[11]. For example, at low powers the hole formation rate may scale quadratically with laser power, whereas at high powers level 2 saturates and the hole formation rate scales linearly with laser power. (This is simply two-photon photochemistry with a resonant intermediate state.) However, in actual situations, signal-to-noise requirements often require that the reading laser power be so large that the quadratic regime cannot be utilized. In addition, the requirement of non-destructive reading makes it desirable to use systems with $\lambda_1 \neq \lambda_2$ permitting complete decoupling of reading and writing processes.

The right half of Fig. 2 illustrates optimized photon-gated PSHB with a four-level system. Here the intermediate state i is distinct from state 2, which allows independent optimization of the level lifetimes. This level structure occurs quite commonly for organic materials in which states 1 and 2 are part of the singlet manifold and level i is the lowest triplet state. The required lifetime τ of level 2 will often be determined by a combination of the required hole width, data rate, and absorption strength. For example, if τ is too short, the holes will be necessarily broad. For efficient gated PSHB the ($2 \rightarrow i$) rate Γ_i should be as large as possible consistent with the requirement that the lifetime of level 2 not be too short. Further, a long intermediate state lifetime τ_i would be advantageous in achieving a large population in level i. It is evident that absorptions $2 \rightarrow$ (a), $1 \rightarrow$ (b), and $i \rightarrow$ (c) involving

photons of frequency ω_1, ω_2, and ω_1, respectively, should not be large in r to prevent undesired bleaching and inefficient excitation of interfering levels. Of course, tne microscopic yield η from the photoreactive levels 3 should be as large as possible for efficient photon-gating.

To date, a number of inorganic and organic examples of photon-gating have been found. The reader is referred to two recent reviews on the subject for references to specific materials[12,13]; only general remarks will be made here. While the inorganic systems are generally crystalline and thus have narrower low-temperature hole widths, the absorption cross section is often low. One outstanding material in this class is actually the first material to show photon-gating: Sm^{2+} ions in BaClF crystals[14]. This material has high gating ratio, and has shown the novel property [15] that holes burned at liquid helium temperatures may be cycled to room temperature for some hours, after which the holes can still be detected after recooling to low temperatures. For the organics on the other hand, the cross section is usually high, but reversibility may be harder to achieve. For one donor-acceptor class of materials [16] consisting of a Zn-tetrabenzoporphyrin derivative with halomethane acceptors in PMMA, fast (8 ns) burning of detectable spectral holes in focused laser spots has been observed[17]. In recent measurements[18], the gating ratio of one member of this donor-acceptor class has been found to *increase* with temperature from a value of $\simeq$100 at 1.6K to $\simeq$10,000 at $\simeq$ 100 K. This is most likely due to the photophysical nature of the one-color hole-burning: at higher temperatures, higher barriers must be surmounted to produce a persistent one-color hole. The photochemical electron-transfer process operative for two-color irradiation is not temperature dependent.

4. OPTIMAL PHOTON-GATED MATERIALS

Using a signal-to-noise analysis similar to that in Sec. 2, the optimal materials properties for photon-gated materials may be derived for the case of frequency-domain readout[10]. One has to again make some assumptions about the performance characteristics of the frequency domain optical storage system, and we follow the considerations of Ref. [5]. We assume that a transmission measurement technique is used for the data readout. Data are encoded in the frequency domain by the presence or absence of narrow spectral holes, each of which represents a characteristic absorption change $\Delta\alpha$, where $\alpha = \sigma_1 N_\omega$ is the absorption coefficient. Here, σ_1 is the low temperature absorption cross section of the frequency-selecting optical transition and N_ω is the concentration of optically active centers that are within a homogeneous linewidth of the laser frequency ω. If N_{tot} is the overall concentration of centers whose resonance frequencies are distributed over the inhomogeneously broadened transition, $N_\omega = (\Delta\omega_h/\Delta\omega_i)N_{tot}$.

A useful quantity for modeling of photon-gated materials is the effective hole-burning yield η_e, which is defined as the relative absorption change $\eta_e = \Delta\alpha/\alpha$, that is produced by

persistent spectral hole-burning during the writing time of 30 ns. Due to the complex nature of gated PSHB processes, the hole-burning yield depends critically on the specific properties of the PSHB material as well as on the writing conditions. It is obvious that it is desirable to optimize the writing conditions to produce the largest yield η_e possible.

For data readout it is essential to discriminate between the optical transmission associated with a spectral hole and the original lower transmission characterizing the absence of a hole. The difference between the two corresponding photocurrents defines the amplitude of the reading signal S that has to be detected,

$$S = e\eta_Q(P/\hbar\omega)\{\exp[-(1-\eta_e)\sigma_1 N_\omega L] - \exp[-\sigma_1 N_\omega L]\}, \quad (2)$$

where P is the laser power impinging on the photodetector, $\hbar\omega$ is the photon energy, L is the thickness of the storage medium, and e is the electronic charge. Assuming shot-noise-limited detection the rms noise current averaged over the reading time τ_R is given by

$$N = \{e^2\eta_Q(P/\hbar\omega\tau_R)[\exp(-(1-\eta_e)\sigma_1 N_\omega L) + \exp(-\sigma_1 N_\omega L)]\}^{1/2}. \quad (3)$$

Eqs. (2) and (3) define the achievable signal-to-noise (voltage) ratio, SNR = S/N. We take SNR = 20 (voltage ratio) in a read time of 30 ns as the minimum value required for a practical storage system. Most of the parameters in Eqs. (2) and (3) are determined by the storage material itself. Thus, Eqs. (2) and (3) can be used to identify suitable combinations of material parameters so that SNR $\geq$ 20.

In principle, the signal-to-noise ratio can be improved by increasing the read power. For simplicity here, we place a reasonable limit on the reading power of 10 mW. Further, we rule out excessive power broadening during readout by choosing a phenomenological limit on the laser power focused on the storage medium: $P \leq 2A\hbar\omega/\sigma_1\tau_R$, where $A = 7.9 \times 10^{-7}$ cm^2 is the laser beam area corresponding to a beam diameter of 10 μm.

With these considerations it is now possible to identify suitable material parameters σ_1, N_ω, L, and η_e which result in SNR $\geq$ 20. It is meaningful to classify materials by a concentration-thickness product $N_\omega L$, as long as the material thickness L does not exceed the depth of field (as given by the Rayleigh range) associated with the focused laser beam of 10 μm diameter, i.e. L $\leq$ 100 μm. Identifying materials by suitable combinations of σ_1 and $N_\omega L$ using the hole-burning yield η_e as a parameter is particularly helpful for establishing guidelines for the search of promising PSHB materials, and this is done in Figure 3. Materials within the shown boundaries for particular values of η_e permit data readout with a signal-to-noise voltage ratio SNR $\geq$ 20 using the reading conditions described above.

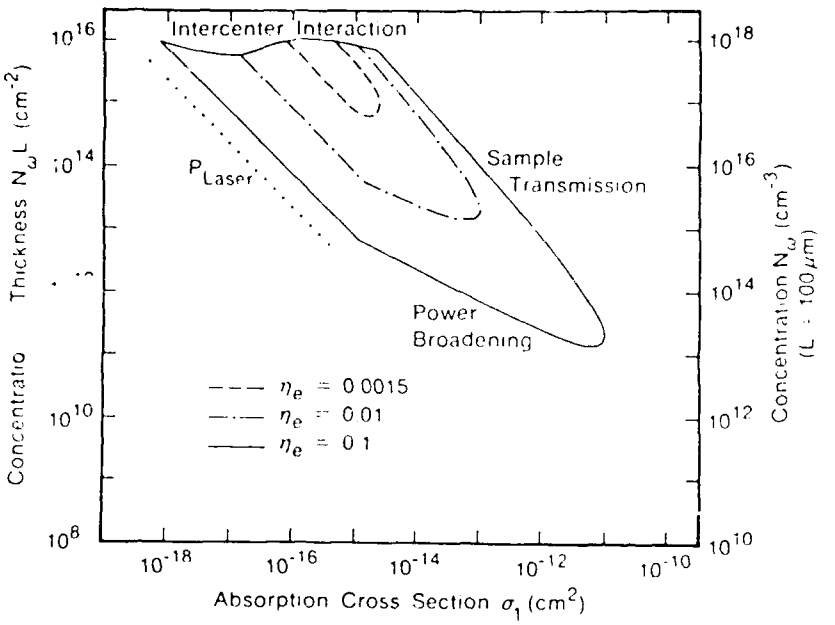

Fig. 3 Materials constraints for gated PSHB materials in order to achieve practical S/N ratios. The various regions and symbols are defined in the text. To illustrate the effect of increased laser power, the dotted line shows the η_e boundary for 100 mW reading power.

It is illustrative to describe the physical meaning of the boundaries in Figure 3. For high cross sections σ_1 and large values $N_\omega L$ the optical absorption becomes very strong. Consequently little light power impinges on the photodetector and the signal-to-noise ratio is low. For high σ_1 and low values $N_\omega L$ the achievable signal-to-noise is limited by the laser power that induces saturation broadening of the spectral holes. For $\sigma_1 \leq 10^{-15}$ cm^2 the available laser power of 10mW is lower than the saturation power and thus defines the SNR limit. At the top of the figure, undesirable interactions between the optically active centers, e.g. energy migration and cooperative excited-state quenching, can restrict the usable concentration of centers; this limit is highly material dependent. With a maximum material thickness of L = 100μm, $N_\omega L$ is ultimately limited to $\sim 10^{16}$ cm^{-2} since the corresponding total concentration of centers N_{tot} approaches the density limit of solid-state materials. In the fabrication of materials containing optically active centers it is usually not a problem to choose very low concentrations. However, in many cases high concentrations of centers are difficult to prepare or are intolerable for physical reasons. The right axis of Figure 3 gives the center concentration N_ω under the assumption that the maximum media thickness L = 100 μm is used.

The results of this analysis clearly show that a suitable PSHB material has to contain a center concentration in excess of 10^{13} cm^{-3}. In case of gated PSHB, the achievable yield η_e depends through complex relationships on the microscopic processes involved in the photo-induced material transformation as well as the amount of write power available for the frequency selective excitation and the subsequent gating process. In addition, spectral

broadening of the produced hole, either by saturation of the transition or by excessive hole-burning, imposes a limit on yield η_e. For this analysis, it seems justified to restrict the hole-burning yield to $\eta_e \leq 0.1$. The $\sigma_1 - N_\omega L$ parameter space shrinks rapidly as η_e decreases. In order to successfully implement a frequency domain optical storage system based on gated mechanisms, it is critical to find a material that permits gated PSHB with very high efficiency in the short writing times required for fast data transfer rates.

5. STATISTICAL LIMITS: STATISTICAL FINE STRUCTURE

A second fundamental limit on PSHB is the recently observed statistical fine structure (SFS) on the inhomogeneous line[7]. SFS arises from the fact that every inhomogeneous profile is actually composed of a large number of discrete homogeneous (Lorentzian) lines that superpose to give an overall Gaussian envelope. Upon close inspection of the inhomogeneous line of pentacene molecules in *p*-terphenyl crystals, it was recently proven by direct observation [7] that a fundamental "spectral noise" (SFS) is present due to number fluctuations in the spectral density of absorbers with optical wavelength.

The source of these fluctuations of the optical absorption with frequency may be understood in the following manner. Due to the randomness associated with the imperfections in the host material, inhomogeneous absorption lines (at least near their centers) are often approximated by smooth, Gaussian profiles[19]. However, since the inhomogeneous line on a microscopic scale is simply a superposition of *discrete* homogeneous lines with widths as much as 1000 times narrower than the overall inhomogeneous profile, the true shape of the inhomogeneous line cannot be a smooth function in reality. In fact, unavoidable number fluctuations in the density of absorbers per unit wavelength interval should give rise to a "spectral noise" on the overall Gaussian background that scales as the square root of the mean number of centers in resonance. To be precise, defining the average number of centers in the probed volume within one homogeneous width of the laser wavelength as $\bar{N}_H$, there should be a statistical fine structure (SFS) present on the absorption profile scaling in absolute magnitude as $\sqrt{\bar{N}_H}$ (in the limit of $\bar{N}_H >> 1$). Since SFS arises from the absorption of many overlapping impurity absorptions, the absolute magnitude of the SFS is clearly larger than a single molecule absorption signal (where $\bar{N}_H \sim 1$).

The recent observations of SFS in the pentacene in *p* terphenyl system were achieved using the highly sensitive, high resolution technique of laser frequency-modulation spectroscopy (FMS) [20] to probe the optical absorption in a zero-background manner sensitive only to narrow spectral features. Furthermore, since its source is a random process, the SFS spectral structure changes for different probe volumes, and an "SFS landscape" of the inhomogeneous line can be generated by acquiring SFS spectra as a function of laser spot position, as in Figure 4.

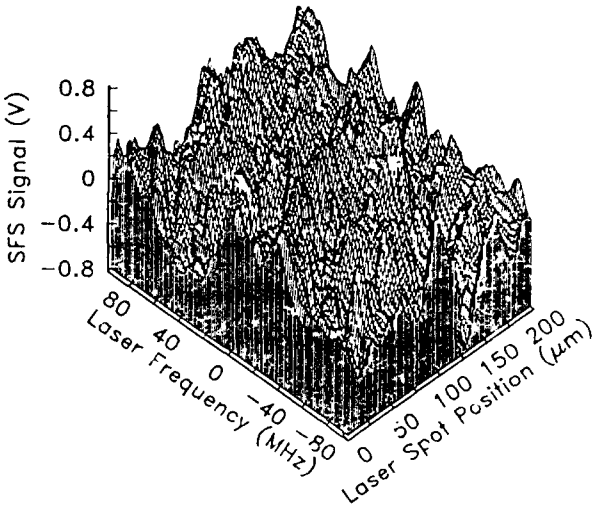

Fig. 4 Surface plot of SFS spectra at different laser spot positions. Each SFS spectrum is the average of 64 scans over the same range of frequencies. A total of 101 spectra were obtained, each with the laser focused to a 20 μm spot on the sample and with the laser spot position displaced by 2 μm along a single spatial axis between spectra.

The bumps and valleys in this figure may be regarded as the "fuzz" on the top of the "haystack" represented by the pentacene inhomogeneous line that results from the statistics of independent, additive random variables. For this data, $\overline{N}_H \sim 10^5$.

The rms amplitude of this spectral structure was observed to scale as the square root of $\overline{N}_H$ [7]. Furthermore, SFS may be used to advantage in that autocorrelation of the measured spectra can provide a measure of the underlying homogeneous width[21]. In recent measurements, SFS has been observed for Nd^{3+} ions in a silica fiber[22,23].

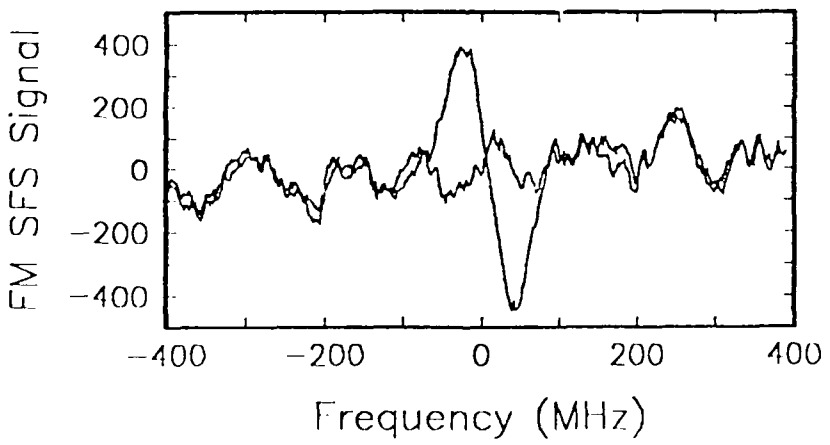

Fig. 5 FM spectra at 1.4 K near the peak of the O_1 absorption at 592.3 nm for pentacene in *p*-terphenyl. The two traces illustrate the structure of the inhomogeneous line before and after the burning of a persistent spectral hole. See Ref. [7].

It is easy to see that SFS represents a fundamental limit on the detectability of shallow spectral features in inhomogeneous lines. To illustrate this, Figure 5 shows a portion of the optical spectrum of pentacene in *p*-terphenyl before and after a spectral hole was burned in the inhomogeneous line. Viewed another way, SFS places a lower limit on the density of absorbers in a frequency domain optical storage system, in order for the signal from spectral holes to be distinguished from the SFS with high reliability[3]. This issue is examined in the next section; for reliable encoding of digital information, the spectral hole should much deeper than the SFS signal.

6. LIMITATIONS ON STORAGE DENSITY DUE TO SFS

The high storage density made possible by PSHB is based on the capability of selectively addressing subclasses of ions or molecules contained in each irradiated spot of recording medium. The stress-induced variations in the local environment of the storage centers are random in nature and consequently centers with a particular resonance frequency are randomly distributed in the host material. As shown above, a tightly focused laser spot may interact with such a small ensemble of centers that statistical number fluctuations on the inhomogeneously broadened line become noticeable. This fundamental source of noise imposes a limit on the achievable storage density for a given concentration of storage centers[3].

The essential requirement is that the number-fluctuation noise be sufficiently smaller than the depth of the written holes so that the required SNR can be obtained for data readout. The number-fluctuation noise is given by $\sqrt{N_\omega V}$, where V is the focal volume in the recording medium, i.e., $V = \pi w_0^2 L$ with where L is active sample thickness and w_0 the radius of the focused beam waist. The sample thickness is approximately limited to the Rayleigh range of the waist, i.e., $L \simeq \pi w_0^2/\lambda$. The achievable areal storage density is approximately given by $D_s \simeq f_\omega/(2w_0)^2$, where f_ω is the storage capacity of the frequency domain ($f_\omega \simeq \Delta\omega_{inh}/\Delta\omega_{hom}$). The relative hole depth $(\Delta N_\omega)/N_\omega$ is given, as before, by the effective hole-burning yield η_e. For each center concentration, the maximum storage density is estimated by applying the condition that the relative hole depth be larger than the relative statistical fluctuations of the number of centers in the volume V by a factor equal to the required SNR value. This is equivalent to requiring that the photon shot noise be larger than the statistical fluctuation noise in the readout signal.

Based on these fundamental considerations, it can be shown readily that for a given center concentration N_{tot}, a maximum storage density of

$$D_s \leq \frac{\pi \eta_e}{4\,SNR_o} \left(\frac{N_{tot} f_\omega}{\lambda} \right)^{1/2} \qquad (4)$$

can be obtained, where SNR_0 is the required value of SNR (voltage ratio).

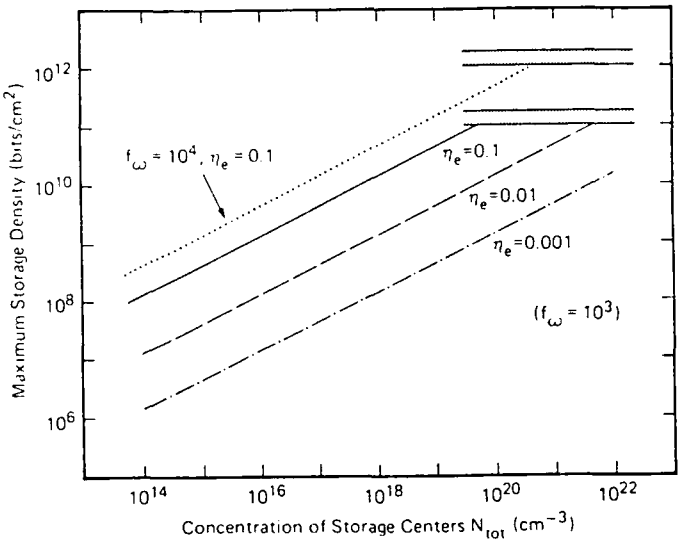

Fig. 6 Maximum storage density in FDOS achievable versus total concentration of centers, with effective yield η_e and frequency-domain storage factor f_ω as parameters.

Figure 6 shows the predictions of Eq. (4) with η_e as a parameter, $SNR_0 = 20$, and $f_\omega = 1000$. For this value of f_ω, the storage density is furthermore limited to $\leq 10^{11}$ bits/cm^2 due to the $\simeq 1\mu$m diffraction limit for the laser beam diameter. The dotted line gives the maximum storage density for $f_\omega = 10^4$ and $\eta_e = 0.1$. These results indicate that it is advantageous to maximize the storage capacity of the frequency domain and the hole-burning yield while keeping the spatial resolution of the focused laser beam at moderate levels. For simplicity, contributions from other noise sources have been neglected for this rather fundamental discussion of statistical noise. Thus, these considerations are applicable to any FDOS configuration independent of the particular readout scheme.

For example, assuming a laser spot size of 10μm diameter and $f_\omega = 1000$ (i.e., a storage density of $\simeq 10^9$ bits/cm^2), minimum center concentrations of $N_{tot} = 5 \times 10^{19}$ cm^{-3}, 5×10^{17} cm^{-3}, and 5×10^{15} cm^{-3} are required for a hole-burning yield of $\eta_e = 0.001$, 0.01 and 0.1, respectively. Comparison of these values with Fig. 3 shows that statistical number fluctuations are not the dominant noise source for this storage density. However, Fig. 6 indicates that very high storage densities in excess of 10^{10} bits/cm^2 can only be achieved with PSHB materials with very high yield and center concentration. In order to achieve a given storage density, a suitable recording material has to also yield sufficient SNR as computed from Eqs. (2) and (3).

6. AN ULTIMATE LIMIT: SINGLE-MOLECULE SPECTROSCOPY IN SOLIDS

A final limit on PSHB is suggested by the recent observations of the optical absorption spectrum of a single impurity center in a solid[8]. As opposed to single ion spectroscopy in vacuum electromagnetic traps[24], in a solid at low temperatures the absorbing center is essentially at rest, confined by the host lattice, and the normal averaging over many "equivalent" centers is removed.

It is certainly within the realm of possibility that in a material with a carefully chosen (gated) hole-burning quantum efficiency, the isolated Lorentzian spectrum of a single absorber could be recorded, the absorber could be induced to undergo a phototransformation that causes its absorption to perhaps move to another wavelength, and the resulting lack of absorption at the original wavelength could be interpreted as information. In preliminary experiments with the extremely weak hole-burning for pentacene in *p*-terphenyl, disappearing single-molecule spectra were observed, though not reliably. It is true that the stochastic nature of the phototransformation for one center introduces considerable uncertainty in the burning time. The possibility of using this effect for storage on a molecule-by-molecule basis, although intriguing, is not actually practical due to the limits on laser spot sizes posed by diffraction. However, if a near-field optical recording scheme could be realized, single-center optical recording might become feasible.

7. CONCLUSION

The limitations on PSHB for FDOS applications resulting from quantum shot noise, power broadening, and number fluctuations can be used to determine the optimal materials parameters for this application. The challenge of molecular engineering is to produce a material satisfying these requirements. On the other hand, alternative configurations for the storage system involving holographic or time-domain readout may alter the required properties. In any case, photon-gating with its built-in threshold would be generally expected to improve performance for all storage applications.

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